Non thermal plasma with metal-organic frameworks (MOFs) for challenging catalytic processes

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Contents

What is plasma used in chemical engineering?

Conventional thermal catalysis *VS* plasma-assisted catalysis

- Extreme operating conditions;
  - High temperature,
  - High pressure;
  - High conversion;
- High energy consumption;
- Well understood mechanism

- Mild operating conditions;
  - Low temperature, non-thermal;
  - atmospheric pressure;
  - Low conversion;
- Low energy consumption;
- **Not well understood mechanism**

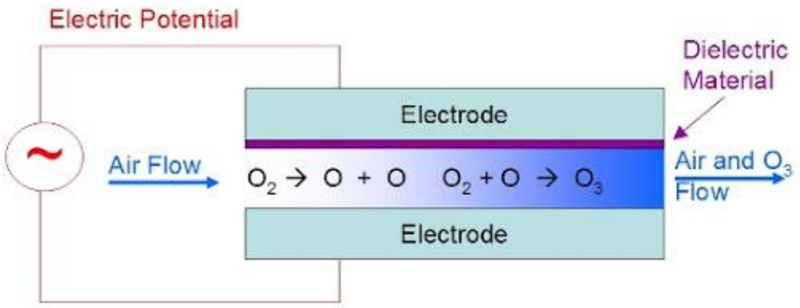
Nonthermal

Atmospheric pressure

Higher energy electrons

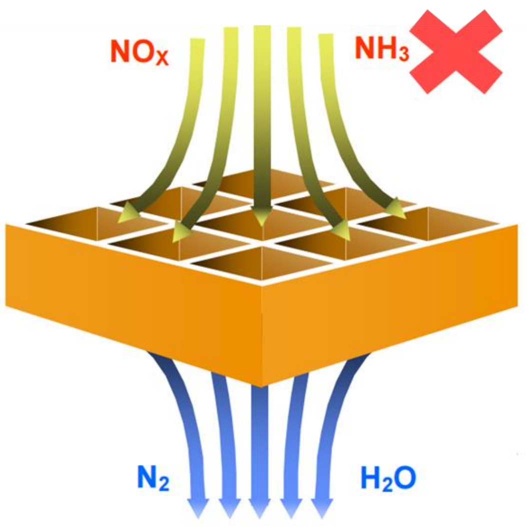
1. Background

Application Areas

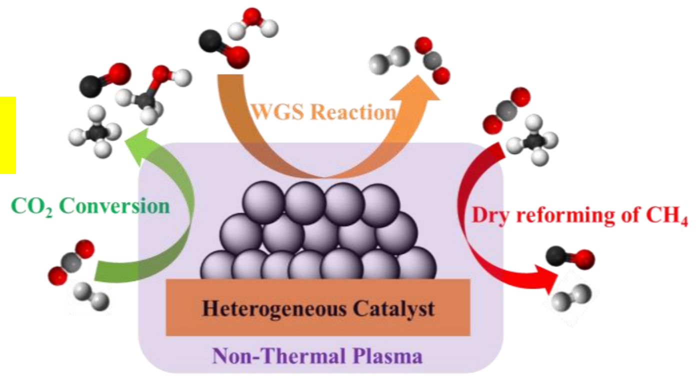


O_3 generation and dissociation

Energy consumption
Reaction Activity
Product Selectivity

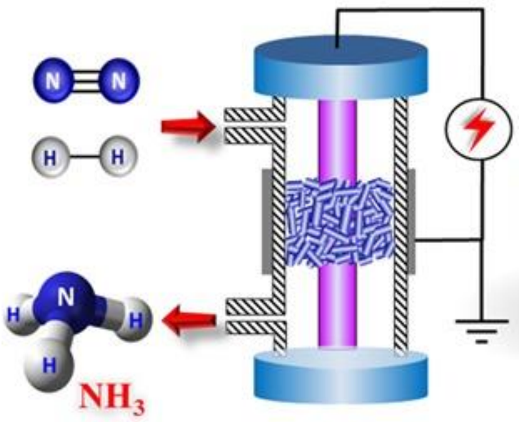


NO_x removal

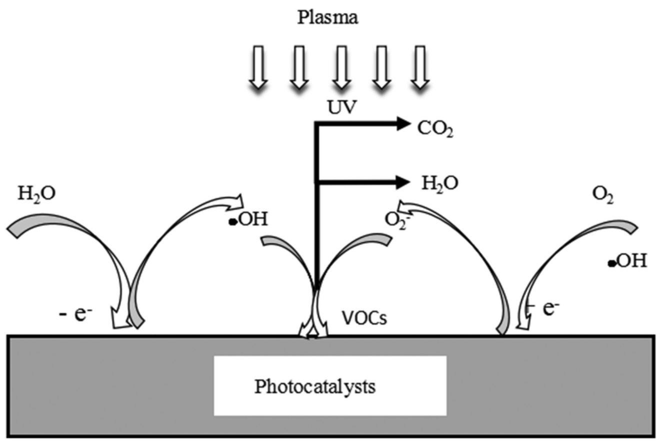


CO_2 Splitting
CO/CO_2 + CH_4 /H_2 /H_2O

C1 chemistry



NH_3 synthesis



VOCs removal

Plasma Process. Polym, 14 (2017) 1600157; *Chin J. Chem Eng.*, (2020); *Chem Eng J*, 258 (2014) 119

2. Combination of Plasma and Porous Catalyst

“**Catalysis**” meaning？

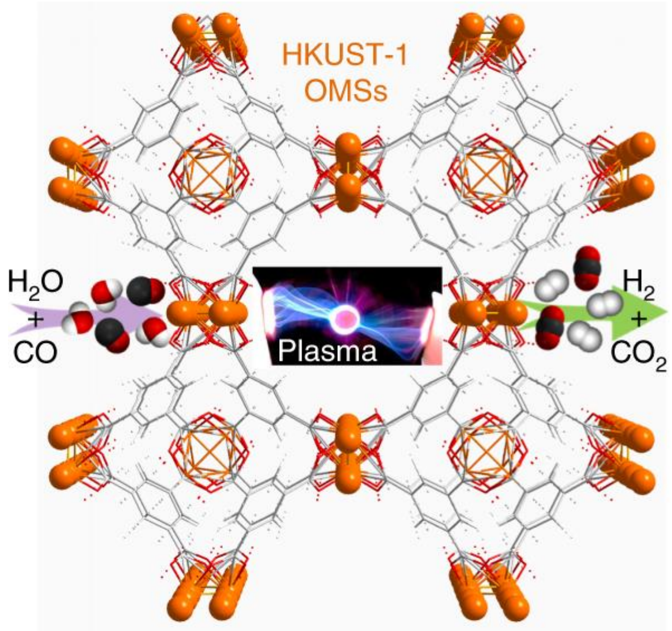
Interaction between Plasma and Catalyst？

Which is more important?

How to decouple?

Non-thermal plasma for water–gas shift reaction (WGSR) using metal–organic frameworks (HKUST-1)

$CO + H_2O \rightarrow CO_2 + H_2$



$Cu_3(BTC)_2$ framework or HKUST-1

Metal nodes: **copper – open metal sites (OMSs)**

Organic linkers: benzene-1,3,5-tricarboxylate (BTC)

Hydrothermal stability: **T < 300 ℃，0 RH%**

Effect of Plasma during the reaction?

Plasma enhance Catalysis vs Catalyst enhance Plasma（OES）

Role of Catalyst?

Active sites（Plasma-DRIFTS）

Non-Thermal Plasma (NTP)
Nonthermal
High energy electrons

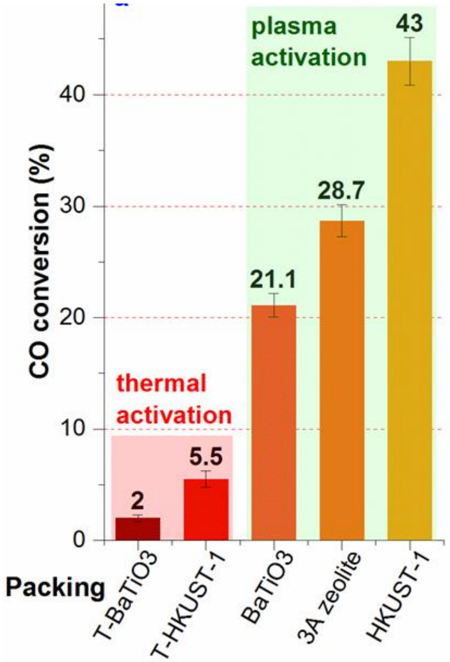
SOLUTION ? →

MOF
Thermal stability
Hydrothermal stability

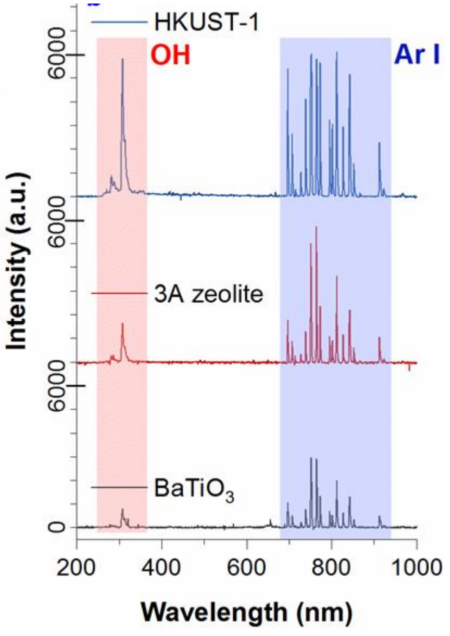
Xu et al,. ***Nature Catalysis***, 2 (2019) 142.

2. Combination of Plasma and Porous Catalyst

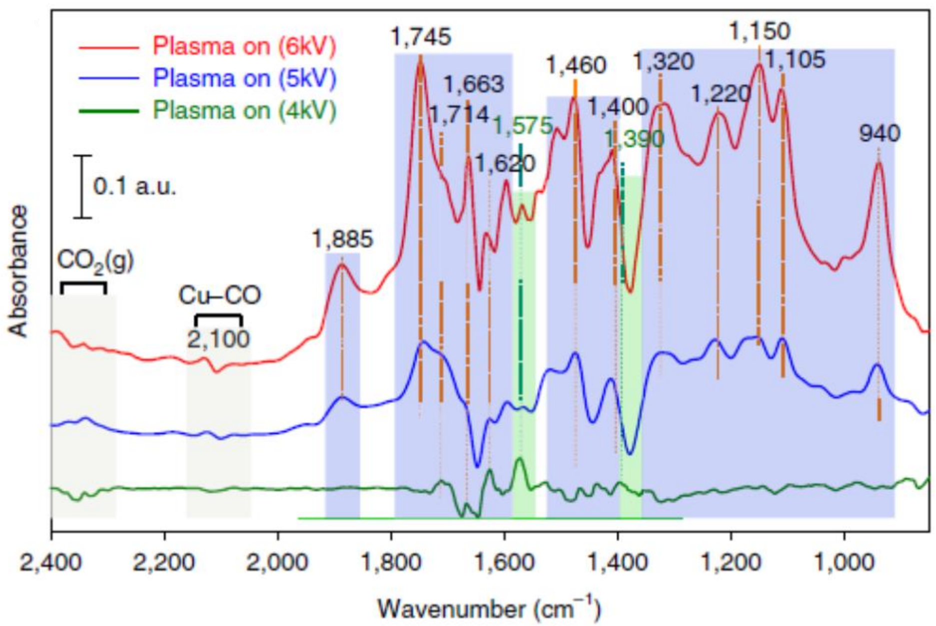
Reaction

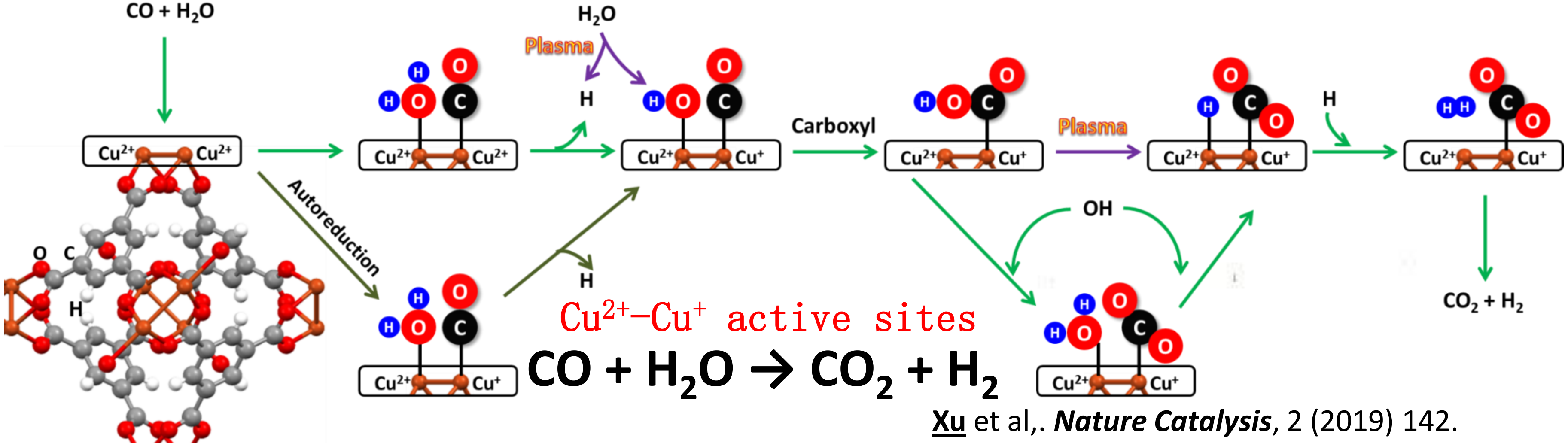


OES



DRIFTS





Cu^{2+}–Cu^{+} active sites

$$CO + H_2O \rightarrow CO_2 + H_2$$

Xu et al,. *Nature Catalysis*, 2 (2019) 142.

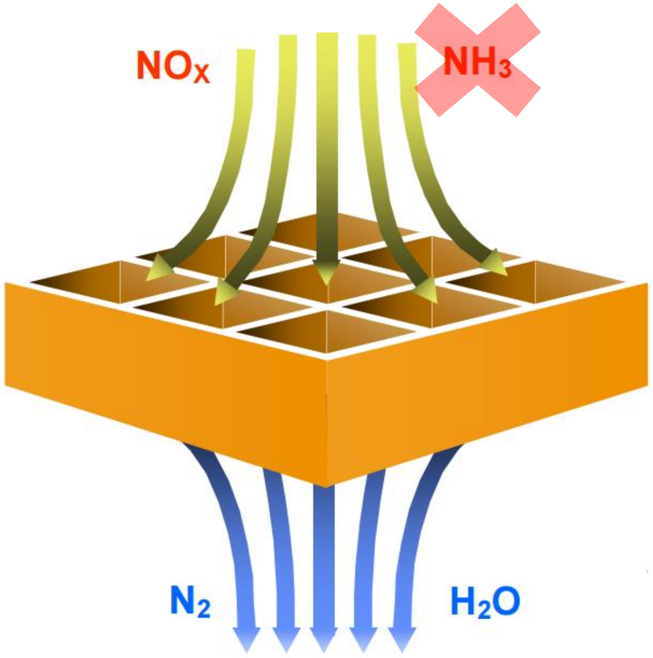
3. Plasma catalysis for DeNOx reaction

Selective Catalytic reduction (SCR)

$$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O$$

$$2\,NO_2 + 4\,NH_3 + O_2 \rightarrow 3\,N_2 + 6\,H_2O$$

< 200 °C
NH_4NO_3



$$2\,NO_2 \xrightarrow[\text{Plasma-assisted}]{\text{Thermal}} N_2 + 2O_2$$

Conventional SCR catalysis

- Extreme operating conditions;
  - High temperature (300-400 ºC),
  - High energy consumption;
- Requiring reducing agent (the release of unreacted ammonia)

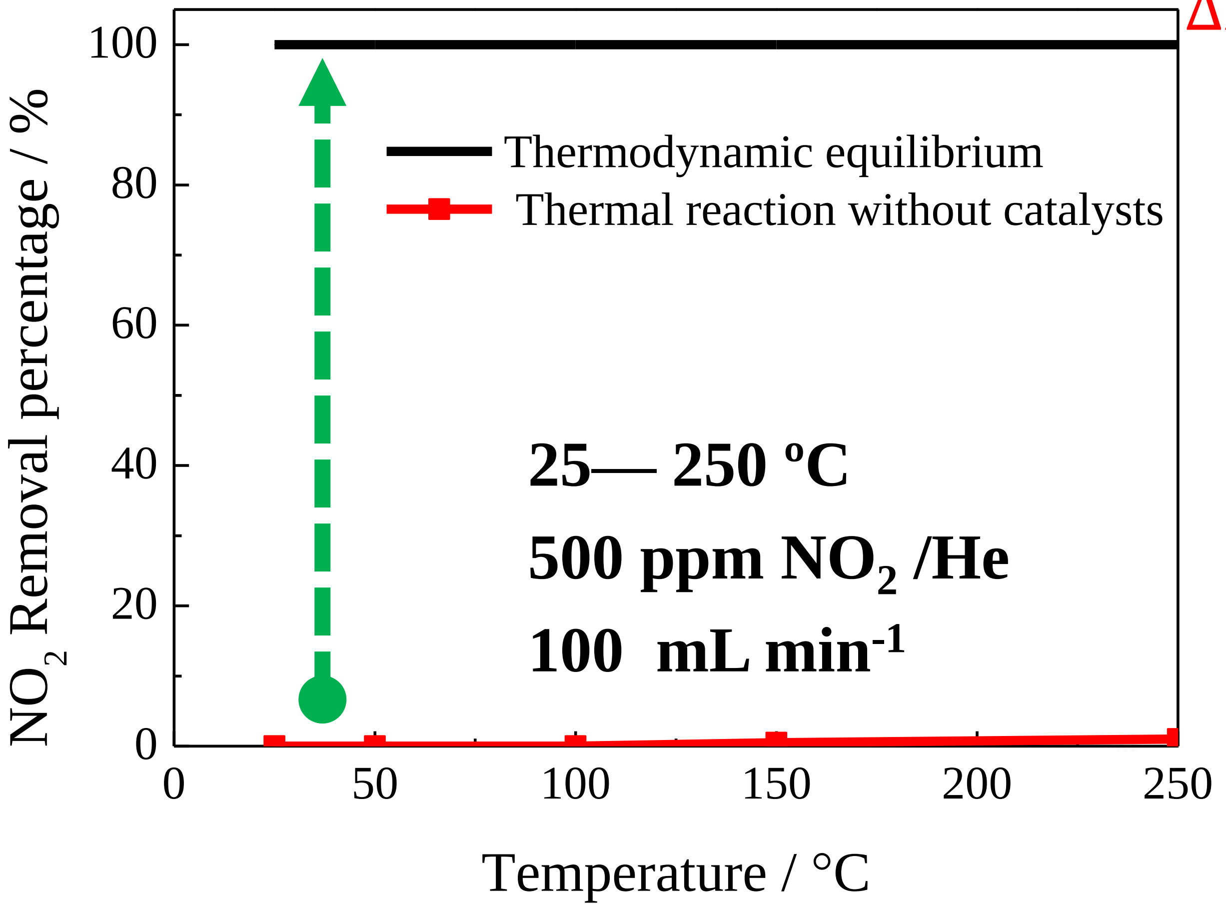
VS Plasma-assisted catalysis

- Mild operating conditions;
  - Low temperature, non-thermal;
  - Low energy consumption
- No reducing agent, one-step dissociation;
- **Few study since 1965, no MOFs catalyst**

Thermal dissociation

$$NO_2 \xrightarrow[\text{Catalysts}]{\text{Thermal}} x\,NO + y\,N_2O + (0.5\text{-}0.5x\text{-}y)\,N_2 + (1\text{-}0.5x\text{-}0.5y)\,O_2$$

$\Delta H^{\circ}_{298\,K} = -33.18$ kJ mol^{-1}

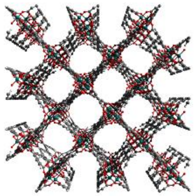


Aim of using plasma-catalysis: 100% NO_2 conversion & selectivity

One-step Adsorption-Conversion of NO_2 using Cu/MFM-300(Al)

$$NO_2 \xrightarrow[\text{Plasma-assisted}]{\text{Thermal}} x\,NO + y\,N_2O + (0.5\text{-}0.5x\text{-}y)\,N_2 + (1\text{-}0.5x\text{-}0.5y)\,O_2$$

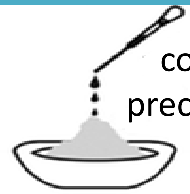
$$NO_2\ \text{Removal}\ (\%) = \frac{n_{NO_2\,in} - n_{NO_2\,out}}{n_{NO_2\,in}} \times 100 \qquad N_2\ \text{Selectivity}\ (\%) = \frac{n_{NO_2\,in} - n_{NO_2\,out} - 2n_{N_2O\,out} - n_{NO\,out}}{n_{NO_2\,in} - n_{NO_2\,out}} \times 100$$



MFM-300(Al) *VS* Al_2O_3, ZSM-5

$Cu(NO_3)_2$/MOFs → **CuO/MOFs** → **Cu/MOFs**

MOFs + precursor solution → Drying → Calcination → Reduction

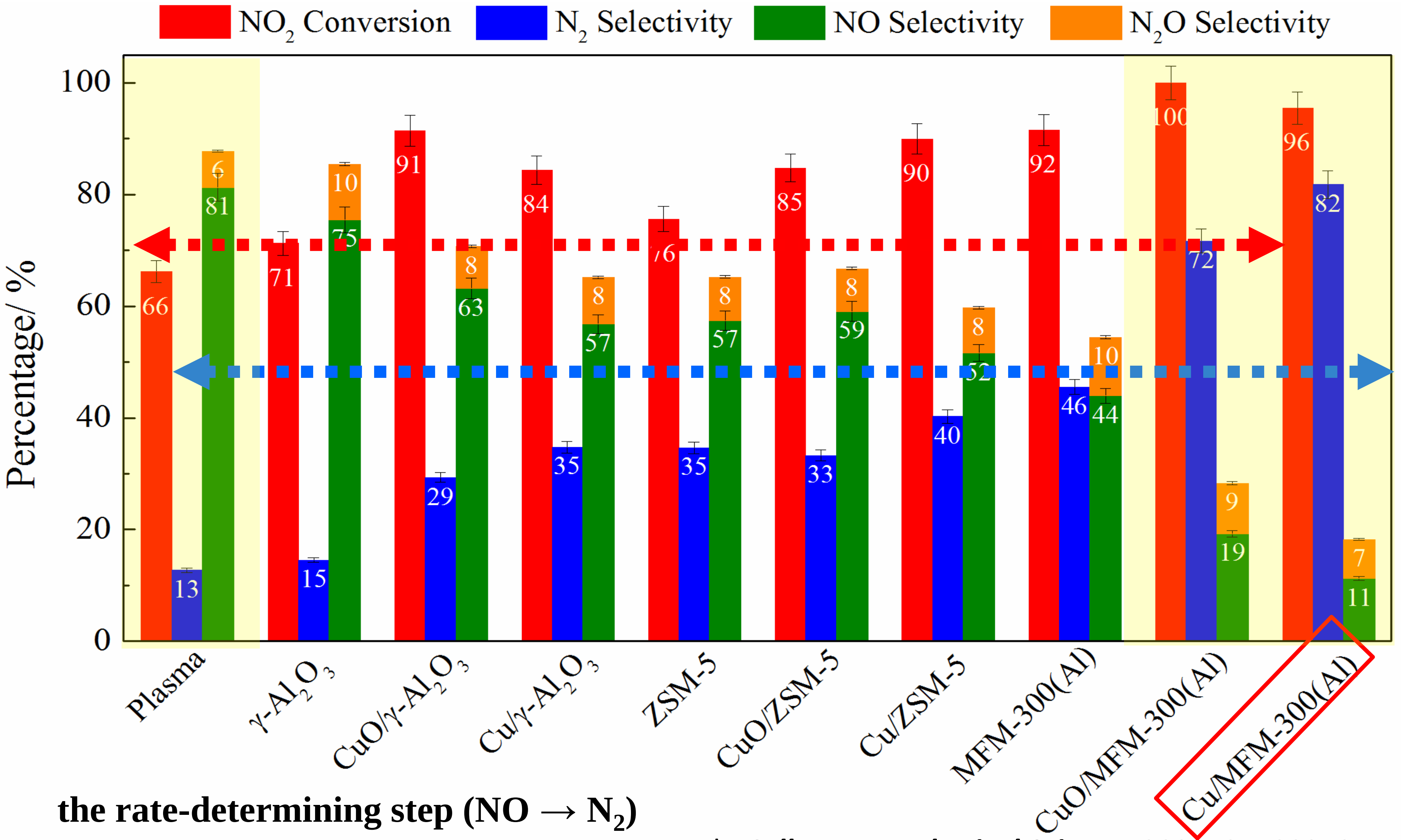


Catalyst synthesis:
Incipient wetness impregnation method

Xu et al., ***Cell Reports Physical Science***, 2021, 2, 100349.

3.3 Non-thermal plasma (NTP) assisted dissociation of NO_2

NTP at 25 °C, 500 ppm NO_2 /He, SEI 0.4 kJ L^{-1}, 240 min

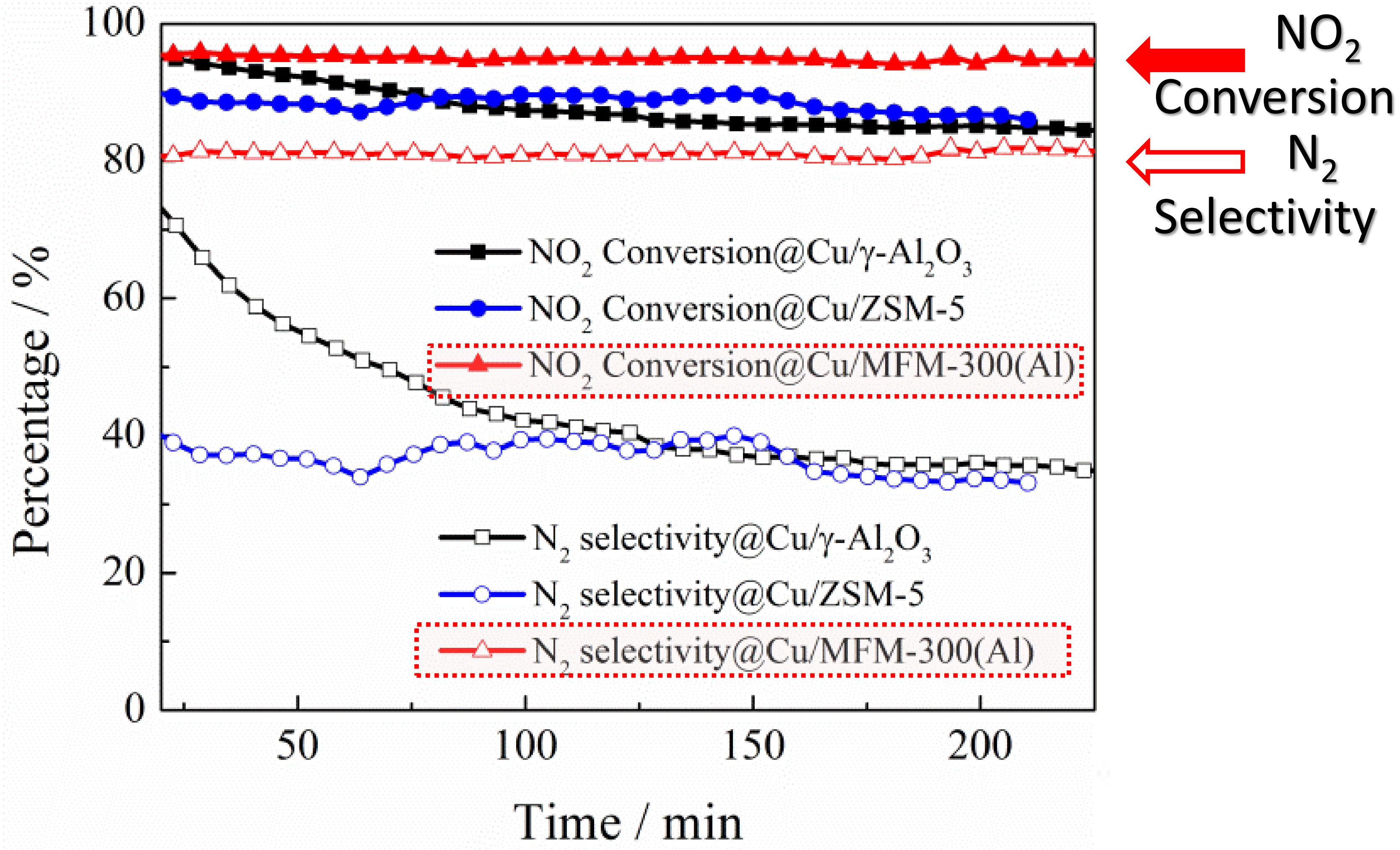


the rate-determining step (NO → N_2)

Xu et al., ***Cell Reports Physical Science***, 2021, 2, 100349.

3.3 Non-thermal plasma (NTP) assisted dissociation of NO_2

NTP at 25 ºC, 500 ppm NO_2 /He, SEI 0.4 kJ L^{-1}, 240 min



The time-dependant ToS plots of NO_2 conversion and N_2 selectivity over various Cu-embedded catalysts for the NO_2 decomposition reaction under NTP conditions.

Comparison of Cu/MFM-300(Al) with the state-of-the-art catalyst

Catayst	Temperature	Space velocity	Volume of catalysts	Total gas flow rate		NO_2 conc.	NO_2 conversion	Weight of catalysts	Cu wt% in the catalyst	Cu Molecular weight	Molar flow of reacted NO_2 substrates	Cu sites	TOF*
	°C	h^{-1}	mL	ml/min	mmol/min	%	%	g	%	g/mol	mmol/h	mmol	h^{-1}
Cu/MFM-300(Al) [this work]	25	150000	0.04	100	4.45	0.050	96	0.05	5.70	63.5	0.13	0.04	2.9
CuO/MFM-300(Al) [this work]	25	150000	0.04	100	4.45	0.050	100	0.05	6.30	63.5	0.13	0.05	2.7
Cu/ZSM-5 [this work]	25	150000	0.04	100	4.45	0.050	90	0.05	7.00	63.5	0.12	0.06	2.2
CuO/ZSM-5 [this work]	25	150000	0.04	100	4.45	0.050	85	0.05	7.00	63.5	0.11	0.06	2.1
Cu/Al_2O_3 [this work]	25	150000	0.04	100	4.45	0.050	84	0.05	8.00	63.5	0.11	0.06	1.8
CuO/Al_2O_3 [this work]	25	150000	0.04	100	4.45	0.050	91	0.05	7.00	63.5	0.12	0.06	2.2
CuO/Al_2O_3 [3]	325	9000	4.00	600	26.68	0.072	30	1.00	35.00	63.5	0.35	5.51	0.1
	520	70020	4.00	4668	207.61	0.126	99	1.00	35.00	63.5	15.54	5.51	2.8
HKUST-1@NTP [4]	25	75000	0.40	500	22.24	0.050	99.87	0.50	32.51	65.5	0.67	2.48	0.3
4 wt.%Cu /ZSM-5 @NTP-H_2 [5]	25	60000	2.00	2000	88.95	0.050	21	0.50	4.000	64.5	0.56	0.31	1.8
	180	60000	2.00	2000	88.95	0.050	60	0.50	4.000	64.5	1.60	0.31	5.2
Cu-SSZ-13 @Thermal-NH_3 [6]	250	30000	0.60	300	13.34	0.035	95	0.13	5.92	63.5	0.27	0.12	2.2
	550	30000	0.60	300	13.34	0.035	83	0.13	5.92	63.5	0.23	0.12	1.9

Comparable to leading NH_3-SCR catalysts using NH_3 at 250-550 °C.

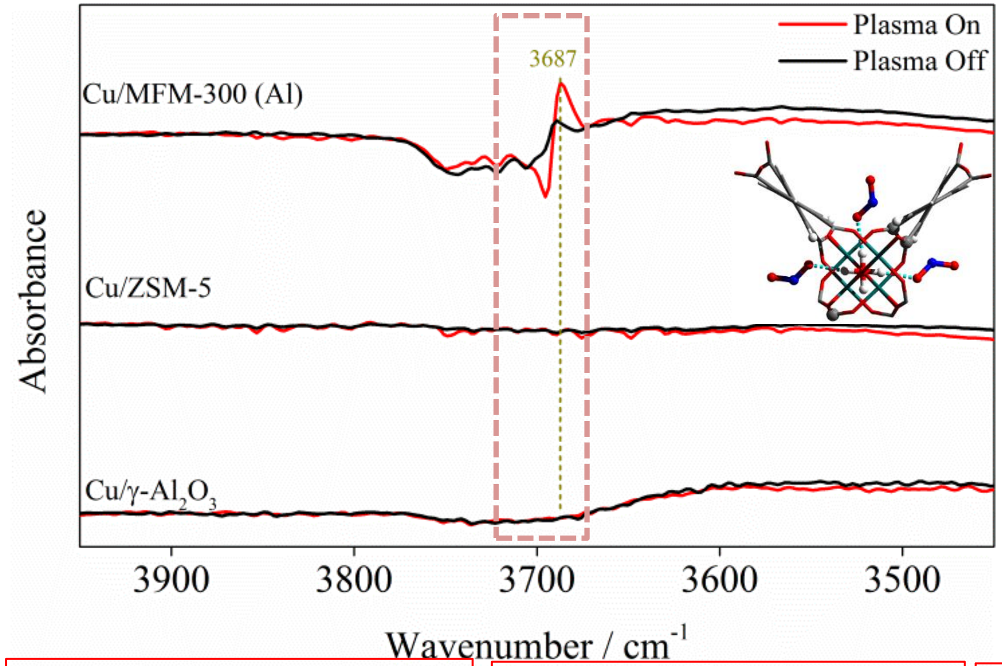
Selective Catalytic reduction (SCR)

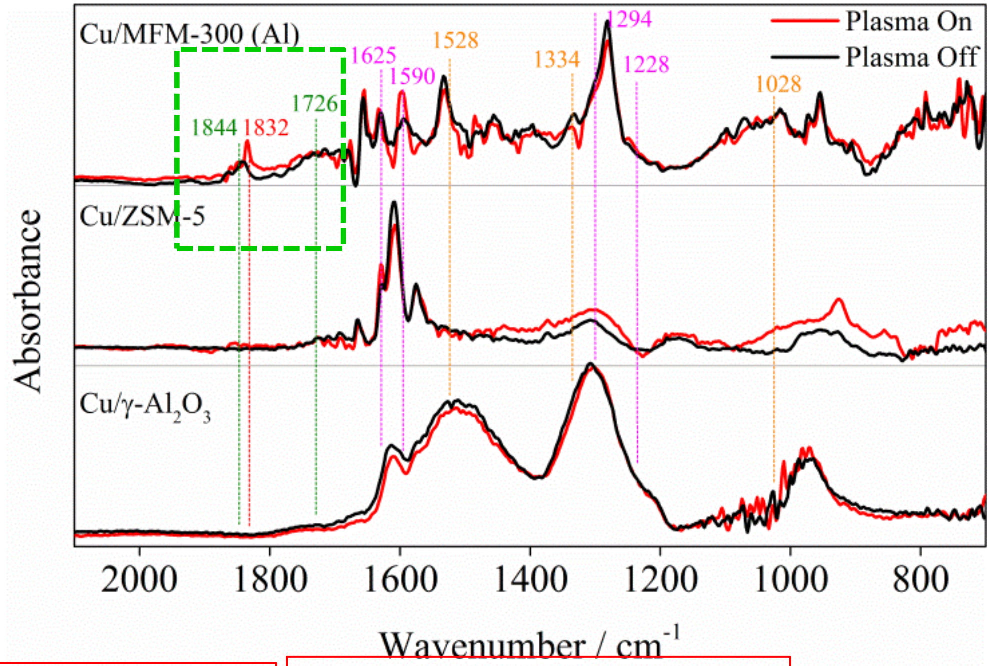
Xu et al., ***Cell Reports Physical Science***, 2021, 2, 100349.

Cu@MOF *vs* Cu@ZSM-5 or Al_2O_3

- *Bare MOF background subtracted*
- *Gas phase NO_2 removed*

NO_2 conversion ↑ & N_2 selectivity↑



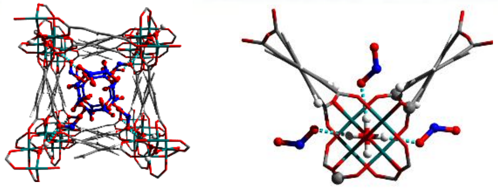


3687 cm^{-1} μ_2–OH stretching retrieval access by NO_2 adsorption	1844 and 1726 cm^{-1} $Cu^{2+}\cdots NO$ nitrosylic adduct complexes	1290 – 1210 cm^{-1} bridged nitrite bands	1620 – 1520 cm^{-1} 1380 – 1330 cm^{-1} 1060 – 980 cm^{-1} surface nitro/nitrate:

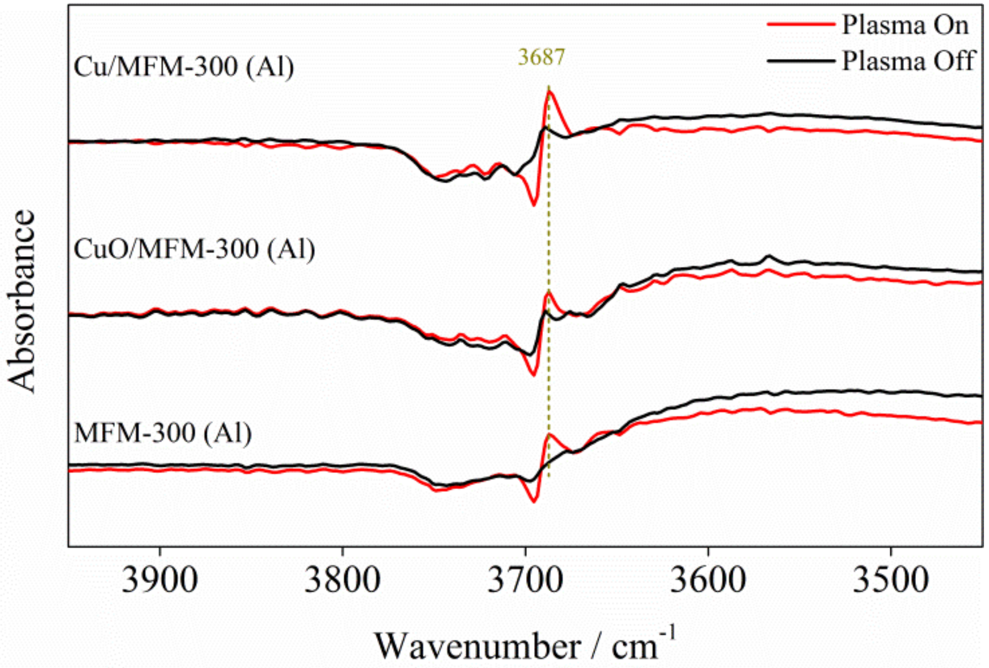
$NO_2 \longrightarrow NO \longrightarrow N_2$

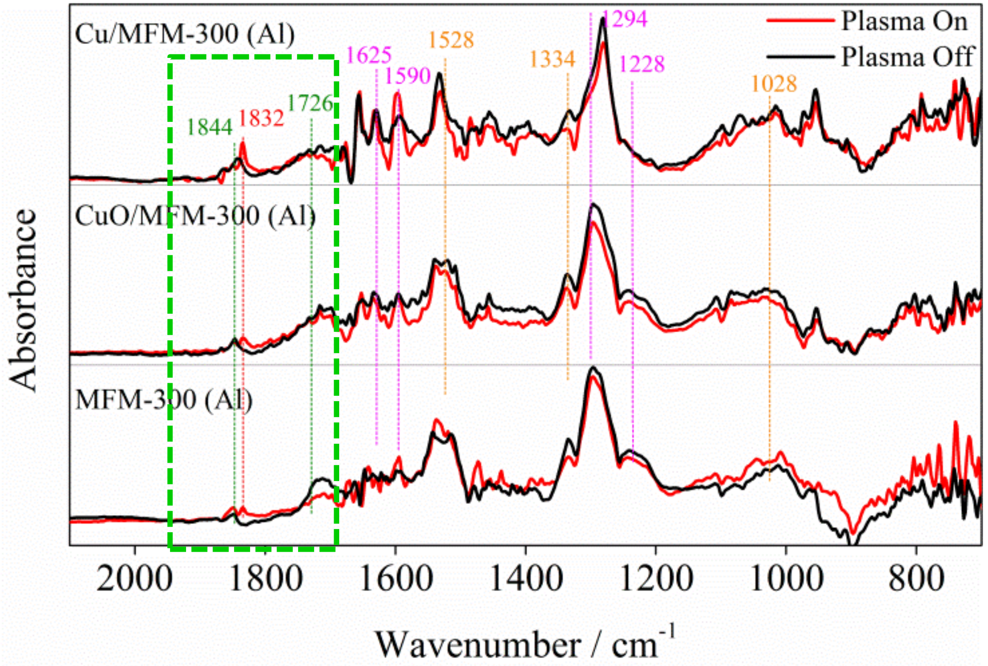
NO_x interaction↑ agree with NO_2 conversion ↑ & N_2 selectivity↑

Cu@MOF *vs* CuO@MOF / bare MOF



N_2 selectivity↑ 82% vs 72% / 46%





3687 cm^{-1}
μ_2–OH stretching retrieval access by NO_2 adsorption

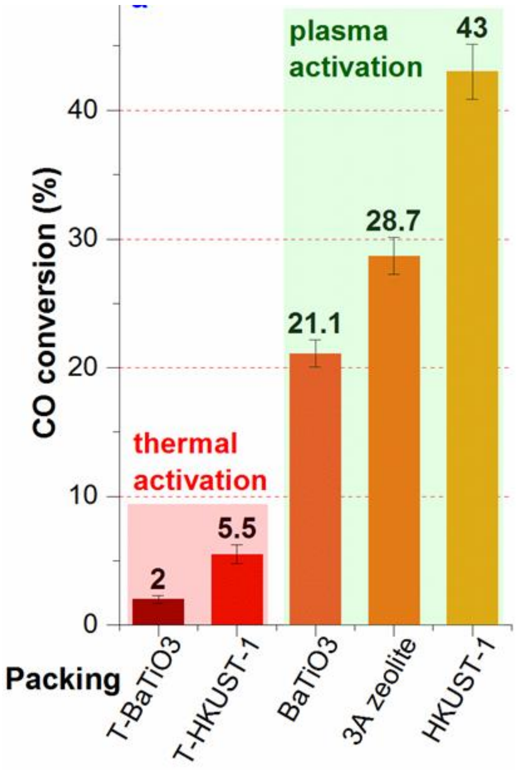
1844 and 1726 cm^{-1}
$Cu^{2+}\cdots NO$ nitrosylic adduct complexes

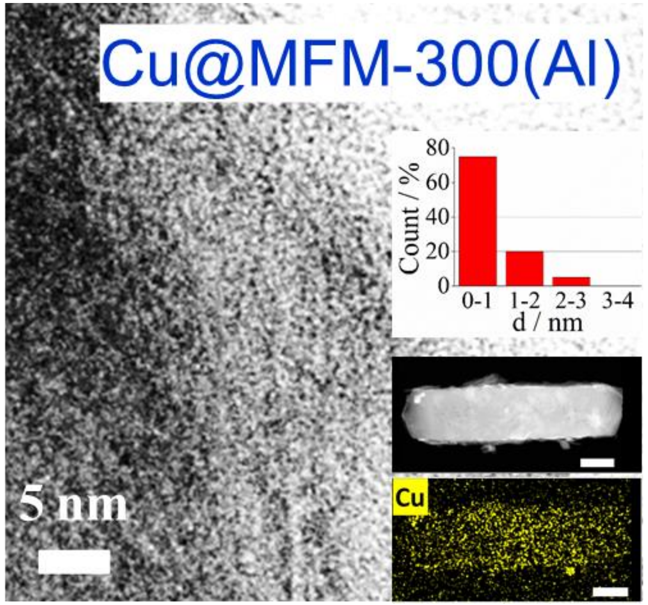
the rate-determining step ($NO \rightarrow N_2$)

μ_2-OH & NO interaction strength agree with N_2 selectivity

Cu/MOF > CuO/MOF > MOF

Plasma-Catalysis Concept: Plasma—MOFs Catalysis





NO_2 conv. 96%
N_2 select. 82%
RT and ATM

Johnson Matthey
Inspiring science, enhancing life

Xu et al, ***Nature Catalysis***, 2019, 2(2), 142

Xu et al., ***Cell Reports Physical Science***, 2021, 2, 100349

Journal of the American Chemical Society, 2021, 143, 29, 10977

CO oxidation on UiO-67 MOFs — ***Journal of Catalysis***, 2020, 391, 522

CO_2 hydrogenation on Ni/UiO-66 MOFs — ***AIChE Journal***, 2020, 66, 16853

Dry reforming of methane on PtNP@UiO-67 — ***Applied Catalysis B: Environmental***, 2020, 260, 118195

- The new concept is generic for other MOFs and other reactions
- Open up new research avenues in exploring the plasma-assisted MOFs-catalysis

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Research Complex at Harwell

MARIE CURIE ACTIONS

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